

## Mechanisms of droplet combustion

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Abstract

The fundamental physico-chemical mechanisms governing droplet vaporization and combustion are discussed. Specific topics include governing equations and simplifications, the classical d<sup>2</sup>-Law solution and its subsequent modification, finite-rate kinetics and the flame structure, droplet dynamics, near- and super-critical combustion, combustion of multicomponent fuel blends/emulsions/suspensions, and droplet interaction. Potential research topics are suggested.

1. Introduction

Research on the gasification, oxidation, and dynamics of fuel droplets commands both practical and fundamental interest to energy and combustion science. On the practical aspect one recognizes that petroleum oil constitutes a significant share of the world energy supply. Since these fuel oils are usually introduced into the combustor as sprays of droplets, it is reasonable to expect that the collective gasification of individual droplets would intimately influence the bulk spray vaporization and oxidation characteristics, which in turn determines the combustor performance. On the fundamental aspect droplet combustion is a problem involving complex chemically-reacting multicomponent two-phase flows with phase change, rich in physical and chemical phenomena typically of interest to the study of aerothermochemistry.

Figures 1a to 1c show some possible droplet combustion modes. In Fig. 1a the fuel droplet is motionless in a stagnant, gravity-free, oxidizing environment of infinite extent. The lack of either forced or natural convection implies that spherical symmetry exists. The basic mechanisms leading to the complete gasification of the droplet are heat and mass diffusion due to the existence of temperature and concentration gradients, the radial convection because of the continuous transfer of mass from the droplet surface to the ambient, and chemical reaction in the flame region. The burning is of the diffusion-flame type in which the outwardly-diffusing fuel vapor and the inwardly-diffusing oxidizer gas approach the reaction zone in approximate stoichiometric proportion. Reaction between them is rapid and intense, implying that the reaction zone is thin and very little reactants can leak through the flame. The chemical heat generated at the flame is transported both outward and inward to heat up the approaching oxidizer and fuel gases in order to achieve ignition. The rest of the inwardly-transported heat is used for droplet heating and to effect liquid gasification.

In the presence of either forced and/or natural convection, a non-radial relative velocity exists between the droplet and the surrounding gas. The shear stress exerted by the gas flow on the surface induces a recirculatory motion within the droplet (Fig. 1b). For higher rates of external convection, flow separation occurs close to the rear stagnation point, creating wake regions both inside and outside of the droplet (Fig. 1c). The presence of the non-radial convection generally enhances the transport rates and thereby the gasification rate, although for sufficiently intense flows the envelop diffusion flame can be extinguished, leading to significant reductions in the gasification rate. It is clear that fluid motion can have strong influence on the combustion process.

The bulk parameters of interest in droplet combustion studies include the droplet gasification rate, the flame location and temperature, the droplet drag, ignition and extinction limits, and the extent of pollutant formation such as that of NO<sub>x</sub>. The droplet diameters of interest are typically between 10  $\mu$ m and 100  $\mu$ m; gasification of smaller droplets can be considered to be instantaneous during the period between spray injection and active combustion, while large droplets either tend to breakup or cannot achieve complete gasification during the available residence time. Droplet breakup also limits its maximum Reynolds number, Re, to about 100 for typical surface tension values of hydrocarbon fuels, Re being defined as the ratio of the characteristic inertia to viscous forces. It may also be noted that it is frequently desirable for the droplets within a spray to have a distribution of sizes and velocities in order to achieve an optimum spatial distribution through penetration as well as a controlled rate of gasification and thereby chemical heat release.

The basic spherically-symmetric, pure-component, droplet combustion model was formulated in the fifties. This model has since been termed the d<sup>2</sup>-Law because it predicts that the

square of the droplet diameter decreases linearly with time. In subsequent years the basic understanding of this model has been extensively revised while other aspects of droplet combustion have also been investigated. Extensive reviews of these developments can be found in Refs. 1 to 3.

The purposes of the present paper are to familiarize the reader with the influence and modeling techniques of chemical reactions in droplet processes, to briefly review current understanding of the basic physico-chemical mechanisms governing droplet combustion, and to suggest potential areas of research. In the next section some frequently-invoked assumptions during droplet combustion modeling are stated and a set of simplified governing equations presented. The  $d^2$ -Law is then derived, and its limitations and subsequent modifications in light of experimental results discussed. This is followed by special topics on finite-rate kinetics, droplet dynamics, high-pressure combustion, multicomponent droplet combustion, and droplet interaction. In Section 9 potential areas of research are suggested.

## 2. Assumptions and simplified governing equations

The general equations governing droplet combustion are those of heat, mass, and momentum conservation, in both the gas and liquid phases, and their coupling at the interface. Auxiliary relations needed are the equations of state and those describing chemical reactions and interfacial phase change. The chemical reactions of interest are usually those of fuel vapor decomposition and oxidation in the gas phase. For very high boiling point fuels, their pyrolysis in the liquid phase may also be of relevance. These equations, for general combustion problems, can be found in the text by Williams.<sup>4</sup>

We shall instead study in the following a simplified system which illustrates the basic diffusive-convective-reactive nature of droplet combustion. The major assumptions are as follows.

- (A1) Diffusion being rate-limiting, although second-order diffusion, that is the Soret and Dufour effects, are neglected.
- (A2) Isobaric processes because of the low Mach number flow.
- (A3) Gas-phase quasi-steadiness. Because of the significant density disparity between liquid and gas, the liquid possesses much inertia such that its properties at the surface, for example the regression rate, temperature, and species concentrations change at rates much slower than those of the gas-phase transport processes. Thus the gas-phase processes can be treated as steady, with the surface boundary variations occurring at longer time scales.
- (A4) Constant gas-phase transport properties. A single binary diffusion coefficient,  $\delta$ , is used for all pairs of species. The specific heat  $C_p$ , the thermal conductivity coefficient  $\lambda$ , and the product  $\rho\delta$ , are assumed to be constants, where  $\rho$  is the density.

With the above assumptions, the gas-phase governing equations are

$$\text{Continuity} \quad \nabla \cdot (\rho \mathbf{u}) = 0 \quad (1)$$

$$\text{Species} \quad \nabla \cdot (\rho \mathbf{u} Y_i - \rho \delta \nabla Y_i) = \dot{w}_i, \quad i=1,2,\dots,N \quad (2)$$

$$\text{Energy} \quad \nabla \cdot (\rho \mathbf{u} C_p T - \lambda \nabla T) = \dot{q} \quad (3)$$

$$\text{State} \quad p = \rho (R\bar{O}/\bar{W})T \quad (4)$$

where  $T$  is the temperature,  $p$  the pressure,  $\bar{W}$  an average molecular weight,  $\mathbf{u}$  the velocity,  $Y_i$  the mass fraction of species  $i$ ,  $\dot{w}_i$  the chemical production rate of  $i$ ,  $\dot{q}$  the chemical heat generation rate, and  $N$  the total number of species.

For each of the equations represented by Eqs. (2) and (3), the first and second terms on the LHS respectively represent convective and diffusive transport, while the RHS is the chemical source/sink term. From chemical kinetics it is well known that the oxidation of a fuel species leading to the formation of products occurs through a complicated sequence of intermediate reactions with a myriad of intermediate species. Thus, for example, the term  $\dot{w}_i$  represents the sum of the mass rates of production and destruction, per unit volume, of species  $i$  from all of the reaction steps.

The adoption of such a detailed kinetic scheme yields immensely complicated expressions for  $\dot{w}_i$  and invariably necessitates the use of numerical solutions. Furthermore, except for the simplest hydrocarbon fuels, the detailed oxidation kinetics of the heavier ones are largely unknown. Thus frequently it is both necessary and useful to approximate the detailed kinetics as a one-step overall reaction between the fuel,  $F$ , and oxidizer,  $O$ , as



where  $\sigma_O$  is the stoichiometric mass coefficient of the oxidizer per unit mass of fuel consumed, and  $Q$  is the associated heat release. The consumption rate of  $F$  can then be expressed as

$$\dot{w}_F = - A \rho_O^a \rho_F^b \exp \left( - \frac{E}{R^* T} \right) \quad (6)$$

which shows that the overall reaction rate is proportional to the concentrations of the reactants and is dependent on the temperature through the Arrhenius factor characterized by an activation energy  $E$ . The exponents  $a$  and  $b$  are the empirically determined reaction orders with respect to the fuel and oxidizer, while  $A$  is the frequency factor which is a measure of the collision frequency between the reactants. Since  $\rho_i = Y_i \rho$ , Eq. (6) can also be expressed as

$$\dot{w}_F = - A \rho^{(a+b)} Y_O^a Y_F^b \exp \left( - \frac{E}{R^* T} \right) \quad (7)$$

Finally, recognizing that in any given reaction the rate of chemical heat release as well as the rates of creation and destruction of all species must be stoichiometrically related, we have

$$\dot{w}_O = \sigma_O \dot{w}_F$$

and (8)

$$\dot{q} = - Q \dot{w}_F$$

for the reaction given by Eq. (5).

Equations (2) and (3) are now well defined. It is clear that the highly non-linear nature of the reaction rate term, which also strongly couples the  $Y_i$  and  $T$  variations, introduces challenging mathematical difficulties and interesting physical phenomena to the problem.

Considerable simplification in the analysis results if one adopts the Shvab-Zeldovich Formulation, which requires

(A5) Unity Lewis number, or  $Le = \lambda / C_p \rho \delta = 1$ .

Thus a linear combination of Eqs. (2) and (3) eliminates the reaction term from all but one of the  $(N+1)$  equations. In particular, if we define a coupling function

$$\Gamma_i = \frac{Y_i}{\sigma_i} + \frac{C_p T}{Q} \quad (9)$$

where  $\sigma_F = 1$ , then Eq. (2) can be replaced by

$$\Gamma_i \text{-Conservation} \quad \nabla \cdot (\rho \underline{u} \Gamma_i - \rho \delta \nabla \Gamma_i) = 0 \quad i=O, F \quad (10)$$

which shows that  $\Gamma_i$  is a conserved scalar during the chemical reaction of Eq. (5). Physically  $\Gamma_i$  represents the sum of the thermal and chemical energies which remains constant when heat and mass are transported at equal rates.

The problem is thus simplified to the solution of the chemically-inert Eq. (10) together with Eq. (3). Sometimes it is possible to first solve for  $\Gamma_i$  such that  $Y_i$ , and thereby Eq. (3), become only a function of  $T$ . The problem is decoupled.

To demonstrate this methodology and be more specific in our discussions, let us further assume

(A6) Spherical symmetry, implying the absence of natural or forced convection.

Then the governing equations become

$$\text{Continuity} \quad \frac{d\tilde{m}}{d\tilde{r}} = 0 \quad (11)$$

$$r_i\text{-Conservation} \quad \tilde{m} \frac{d\tilde{r}_i}{d\tilde{r}} - \frac{d}{d\tilde{r}} \left( \tilde{r}^2 \frac{d\tilde{r}_i}{d\tilde{r}} \right) = 0 \quad i=O, F \quad (12)$$

$$\text{Energy} \quad \frac{\tilde{m}}{r^2} \frac{d\tilde{T}}{d\tilde{r}} - \frac{1}{r^2} \frac{d}{d\tilde{r}} \left( \tilde{r}^2 \frac{d\tilde{T}}{d\tilde{r}} \right) = D\tilde{T}^{-(a+b)} Y_O^a Y_F^b \exp \left\{ -\frac{E}{R^0} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right\} \quad (13)$$

where  $r$  is the radial co-ordinate,  $s$  indicates the surface,  $\tilde{m}=(\rho u r^2)/(\rho \delta r_s)$ ,  $\tilde{r}=r/r_s$ ,  $T=C_p T/Q$ ,

$$D = \left\{ \frac{r_s^2}{\rho \delta} \right\} \left\{ A \left( \frac{C_p \rho \tilde{w}}{Q R^0} \right)^{(a+b)} \right\} \exp \left( -\frac{E}{R^0 T_r} \right)$$

is the ratio of the characteristic flow time to the characteristic reaction time, and  $T_r$  is a characteristic temperature in the reaction zone.

Equation (11) shows that

$$\tilde{m} = \text{constant} \quad (14)$$

implying that the mass flow rate is a constant as it should be.

Equations (12) and (13) are to be solved subject to the boundary conditions

$$\text{At } \tilde{r} = \infty: \quad Y_O = Y_{O\infty} \quad (15)$$

$$Y_F = 0 \quad (16)$$

$$\tilde{T} = \tilde{T}_\infty \quad (17)$$

$$\text{At } \tilde{r} = 1: \quad dY_O/d\tilde{r} = \tilde{m} Y_O \quad (18)$$

$$dY_F/d\tilde{r} = -\tilde{m}(1-Y_F) \quad (19)$$

$$d\tilde{T}/d\tilde{r} = \tilde{m} L/Q \quad (20)$$

$$\tilde{T} = \tilde{T}_s \quad (21)$$

where  $L$  is the latent heat of gasification. Equations (18) and (20) respectively state that oxidizer does not penetrate into the surface, and that all the heat conducted to the droplet is used for gasification. Equations (15) to (21) constitute seven boundary conditions to solve for the three second order differential equations, Eqs. (12) and (13), together with the burning rate parameter  $\tilde{m}$ .

Solving Eq. (12), we have

$$\left( \frac{Y_O}{\sigma_O} + \tilde{T} \right) = \left( \frac{Y_{O\infty}}{\sigma_O} \right) e^{-\tilde{m}/\tilde{r}} - \beta (1 - e^{-\tilde{m}/\tilde{r}}) + \tilde{T}_\infty \quad (22)$$

and

$$(Y_F + \tilde{T}) = (1 - \beta) (1 - e^{-\tilde{m}/\tilde{r}}) + \tilde{T}_\infty \quad (23)$$

where

$$\beta = \frac{C_p (T_\infty - T_s) + L}{Q}$$

Thus the problem is reduced to the solution of Eq. (13) for  $\tilde{T}$ , with  $Y_O$  and  $Y_F$  given by Eqs. (22) and (23).

### 3. The $d^2$ -Law and its modifications

A particularly simple solution exists if we make the following assumption.

- (A7) Reaction proceeds with an infinitely fast rate at an infinitesimally-thin flame located at  $\tilde{r}_f$ , implying that both reactants are totally consumed there.

Thus we have

$$Y_O = Y_F = 0, \quad \tilde{T} = \tilde{T}_f, \quad \text{at } \tilde{r} = \tilde{r}_f \quad (24)$$

Furthermore, since there is now no leakage of the reactants through the flame, the oxidizer concentration is identically zero in the inner region to the flame. Thus, in particular, at the droplet surface we have

$$Y_O = 0 \text{ at } \tilde{r} = 1 \quad (25)$$

Applying Eqs. (24) and (25) to Eqs. (22) and (23), we obtain three equations from which the three parameters of practical interest, namely the burning rate  $\tilde{m}$ , the flamefront standoff ratio  $\tilde{r}_f$ , and the flame temperature  $\tilde{T}_f$ , can be solved as

$$\tilde{m} = \ln(1+B) \quad (26)$$

$$\tilde{r}_f = \frac{\tilde{m}}{\ln(1+Y_{O\infty}/\sigma_O)} \quad (27)$$

and

$$\left\{ \frac{C_p(T_f - T_\infty)}{Y_{O\infty}/\sigma_O} \right\} + \{ L + C_p(T_f - T_s) \} = Q \quad (28)$$

$$\text{where } B = \frac{C_p(T_\infty - T_s) + (Y_{O\infty}/\sigma_O)Q}{L} \quad (29)$$

is a transfer number representing the ratio of the "driving force" for vaporization to the "resistance" to vaporization. The chemical source term,  $(Y_{O\infty}/\sigma_O)Q$ , is usually much greater than the thermal term,  $C_p(T_\infty - T_s)$ . Equations (26) to (28) show that  $\tilde{m}$ ,  $\tilde{r}_f$ , and  $T_f$  are constants for a given fuel-oxidizer system.

Finally, further assume that

- (A8) Fuel vaporization rate at surface is equal to fuel consumption rate at flame  $\dot{m} = 4\pi\rho_L r_s^2$ .

Then

$$-\frac{d}{dt} \left( \frac{4}{3} \pi \rho_L d_s^3 \right) = \dot{m} \quad (30)$$

which is simply

$$\frac{d(d_s^2)}{dt} = -K \quad (31)$$

with

$$K = \frac{8\rho_L \delta}{\rho_L} \ln(1+B) \quad (32)$$

where  $\rho_L$  is the liquid density. The parameter  $K$  is known as the evaporation or burning rate constant.

Integrating Eq. (31) yields

$$d_s^2 = d_{s0}^2 - Kt \quad (33)$$

which forms the basis of the  $d^2$ -Law.

Setting  $d_s = 0$ , we obtain the total burning time as

$$\tau = \frac{d_{s0}^2}{K} \quad (34)$$

Equation (34) shows that  $\tau$  varies quadratically with the initial droplet size, hence demonstrating the basic principle of atomization in order to achieve rapid gasification.

It is also of interest to note that in Eq. (28) we have expressed  $T_f$  in such a way as to illustrate the fact that it is just the adiabatic flame temperature for the stoichiometric reaction between the liquid fuel and the oxidizer-inert mixture. That is, the amount of heat release,  $Q$ , by burning unit mass of fuel is used (a) to gasify the fuel and heat the fuel vapor from  $T_s$  to  $T_f$ , and (b) to heat  $(Y_{O_2}/\rho_0)^{-1}$  amount of the oxidizer mixture from  $T_\infty$  to  $T_f$ .

Figure 2a shows the  $d^2$ -Law temperature and concentration profiles, which are typical of diffusional burning.

Because of its simplicity, the  $d^2$ -Law has been extensively used in modeling droplet and spray combustion. In particular, the qualitative behavior of Eq. (33) has been found to be largely correct while the burning rate constant can generally be predicted to within a factor of two, allowing for the uncertainty in selecting transport property values.

However, experiments<sup>5,6</sup> on spherically-symmetric droplet combustion reveal certain qualitatively different behaviors, indicating the existence of serious weaknesses in the  $d^2$ -Law. Figure 3 shows that, immediately after ignition, there exists a short period during which  $d_s^2$  practically does not change. Furthermore, rather than a constant,  $\bar{r}_f$  increases significantly after ignition. In a low- $Y_{O_2}$  environment the increase persists until burnout, while in a high- $Y_{O_2}$  environment  $\bar{r}_f$  levels off toward the latter part of the droplet lifetime.

Both of these deviations are consequences of initial conditions which are not included in the  $d^2$ -Law. The initial slow rate of surface regression is primarily due to the need to heat up the initially cold droplet to a temperature hot enough to sustain steady burning; frequently this temperature is close to the liquid's boiling point under the prevailing pressure. During this period most of the heat generated is used for droplet heating instead of gasification, thereby resulting in a slow surface regression rate. The droplet also expands as it is heated up, hence compensating for the reduction in the droplet size from gasification.

Since active droplet heating and intense gasification are somewhat mutually exclusive, droplet heating is mostly over in about the first 10% of the droplet lifetime. For the remaining period  $d_s^2$  should vary approximately linearly with time. During multicomponent droplet combustion or high-pressure combustion the droplet heating period can be considerably longer, as will be discussed later.

To model droplet heating one may simply include in the latent heat of vaporization,  $L$ , an additional amount representing the heat conducted into the droplet interior. This amount can then be determined by solving the temperature distribution within the droplet.<sup>7,8</sup>

The observed behavior of  $\bar{r}_f$  can be explained by the fact that the fuel vapor present in the region between the droplet and the flame continuously change as the droplet and flame sizes change. The significance of this variation can be appreciated by considering a droplet immediately after it is ignited. At that instant the amount of fuel vapor present in the inner region should be of the same order as the amount present in the droplet vicinity before ignition. Since this amount is very small because of the low droplet temperature, the flame initially must lie close to the droplet surface. With subsequent gasification the fuel vapor present in the inner region increases and larger flames can be supported. Therefore only part of the fuel vaporized during this period is consumed at the flame, the rest is being accumulated in the inner region as the flame expands. This amount may also become depleted toward the latter part of the droplet lifetime.

It is reasonable to expect that the accumulated amount is significant because although the gas density is low compared with the liquid density, the flame size can be substantial such that volume effect dominates. Furthermore the fuel vapor is accumulated at the expense of the finite droplet mass. Indeed it is easy to demonstrate<sup>6</sup> that the amount of the fuel vapor present, as given by results of the  $d^2$ -Law, is of the same order as the droplet mass.

The existence of this accumulation process implies that mass conservation is actually violated in  $d^2$ -Law. Rather, overall mass conservation for the fuel vapor should read,

- Gasification rate at droplet surface
- = Consumption rate at flame
- + Accumulation/Depletion rate in the inner region

(35)

The last term is absent in the  $d^2$ -Law.

When the accumulation process is included in the formulation<sup>6</sup>, then the experimentally observed behavior of  $\dot{r}_f$  is predicted. The result that  $\dot{r}_f$  does approach a constant value for burning in high  $Y_{O_2}$  environments can also be explained by its relatively smaller flame size, which requires less fuel vapor for accumulation.

An important practical implication of fuel vapor accumulation is that since the fuel gasification rate is not equal to the fuel consumption rate, adoption of the  $d^2$ -Law in spray modeling may result in grossly erroneous estimates of the bulk chemical heat release rate. In particular, in a low-oxidizer environment some fuel vapor is still left behind upon complete droplet gasification, as shown in Fig. 4.

#### 4. Finite-rate kinetics and the flame structure

It is perhaps somewhat remarkable that because of the basic diffusive nature of droplet combustion, much can be learned by making the flame-sheet approximation without having to consider the detailed reaction kinetics. There are, however, certain phenomena in which the chemical reaction rate can be of the same order as the diffusion rate in parts of the flow field. They can only be described by allowing for finite-rate kinetics and thereby resolving the flame structure. Important examples are the determination of the ignition/extinction limits and the combustion of monopropellant droplets.

To resolve the flame structure, it is necessary to solve Eq. (13) with the reaction term, which is governed by the Damköhler number  $D$  and the activation energy  $E$ . For reactions of interest to combustion  $E$  usually assumes a large value, of the order of 20 to 100 kcal/mole. Thus the Arrhenius factor  $\exp(-E/RT)$  is a very sensitive function of temperature. It assumes the maximum value at the location of the maximum temperature in the flow field. However, by moving slightly away from this location, the slight decrease in the temperature can significantly reduce the magnitude of the Arrhenius factor and thereby effectively freeze the chemical reaction.

Thus the flow field can be considered to consist of a narrow reaction region separating two broad chemically-frozen regions in which fuel and oxidizer diffuse toward each other. Furthermore, since the gradients of the flow properties are very steep within the narrow reaction region, diffusion dominates over convection and therefore balances the reaction term. On the other hand in the frozen regions diffusion balances convection. Finally, since reaction proceeds at a finite rate, the reactants cannot be completely consumed within the flame and therefore may leak through it. This leakage represents incomplete fuel utilization and in severe cases can lead to extinction. The general temperature and concentration profiles are shown in Fig. 2b.

A solution of Eq. (13) usually yields an S-shaped multi-valued curve when a relevant parameter, say  $\bar{m}$ , is plotted versus  $D$  (Fig. 5). This S-curve can be interpreted as follows.

For  $D = 0$ , the flow is chemically frozen everywhere and we retrieve the pure vaporization state. By gradually increasing  $D$  along the lower branch, weak chemical reaction is possible leading to slight increases in  $\bar{m}$ . However, with continuous increase in  $D$  a value  $D_I$  will be reached beyond which the only possible solution lies on the upper branch. Thus at  $D_I$  the system changes abruptly from the lower to the upper branch, which represents all the possible burning states. In particular as  $D \rightarrow \infty$  we retrieve the flame-sheet solution. Therefore this lower turning point can be identified as the ignition state and  $D_I$  an ignition Damköhler number. Similarly if we continuously decrease  $D$  along the upper branch, then beyond  $D_E$  steady burning ceases to be possible and only the lower branch has solutions. Therefore the upper turning point can be identified as the extinction state and  $D_E$  an extinction Damköhler number.

Physically, the non-existence of solutions implies that the chemical reaction rate cannot balance the heat transport rate. Thus for the lower branch, beyond  $D_I$ , the chemical heat is generated so fast in the reaction region close to the hot, oxidizing, ambience that they cannot be transported away in a steady manner. This leads to an increase in the reaction zone temperature and thereby further increase in the reaction rate, culminating in the runaway event of ignition. This feed-back mechanism proceeds extremely rapidly because of the highly temperature-sensitive Arrhenius kinetics.

Similarly, for the upper branch, the effects of the finite reaction rate are that the flame is broadened and both fuel and oxidizer can now leak through the flame zone. Thus with excessive leakage the chemical heat release cannot keep up with the heat transported

away from the flame zone, leading to a precipitous drop in the flame temperature and thereby extinction.

Equation (13) has been formally solved using the newly-developed technique of large activation energy asymptotic technique.<sup>9,10</sup> The diffusive-reactive and diffusive-convective regions are separately solved and matched, using the ratio of the thermal energy in the reaction region to the activation energy as the small parameter of expansion. The S-curve is reproduced and explicit expressions derived for the ignition and extinction states. These criteria are useful in assessing the combustibility of a given droplet-oxidizer system.

Finite-rate kinetics is also essential in the study of monopropellant droplet combustion. Unlike conventional hydrocarbon fuels which burn through diffusion flames, a monopropellant contains both fuel and oxidizer. Thus after gasification the outwardly-transported gas is a premixed combustible, which will eventually burn as a premixed flame. While a detailed discussion of the structure of premixed flames is outside the scope of this paper, it may be noted that studies<sup>4</sup> have shown that for large droplets the burning resembles that of one-dimensional premixed flame, with

$$\frac{d(d_s)}{dt} = \text{constant},$$

while for small droplets the burning resembles that of the conventional fuel droplet, with

$$\frac{d(d_s^2)}{dt} = \text{constant}.$$

## 5. Droplet dynamics

The heat and mass transfer processes of the spherically-symmetric droplet combustion discussed so far are closely influenced by the droplet dynamics, and vice versa. As mentioned previously, while increasing non-radial convection generally increases the gas-phase transport rates and thereby the burning rate, there exists an upper limit in the convection intensity at which the flame can be blown off, that is extinguished. Various semi-empirical correlations have been proposed for the burning rate augmentation due to convection, such as<sup>2</sup>

$$\frac{K}{K_{s.s.}} = \left\{ 1 + \frac{0.278 \text{ Re}^{1/2} \text{ Pr}^{1/3}}{(1 + 1.232/\text{RePr}^{4/3})^{1/2}} \right\} \frac{\ln(1+B)}{B} \quad (36)$$

where  $K_{s.s.}$  is the spherically-symmetric result. Systematic theoretical and experimental investigation on the blow-off of the droplet flame have also been conducted. In particular criteria governing the blow-off limits have been determined.<sup>11</sup>

Combustion can influence the droplet drag and therefore its dynamics in three essential ways. The outward mass flux at the droplet surface reduces friction drag but increases pressure drag because of early separation. The net result is as yet unclear. The existence of the interfacial velocity, especially after the droplet has been substantially heated up, may delay separation and hence reduce both the friction and pressure drag. Finally, the significant elevation of the temperature in both the gas and liquid phases, and the increase in the gas density because of the presence of the high-molecular-weight fuel vapor, can all greatly influence the fluid properties and therefore the drag coefficient. The above factors have not been systematically investigated.

In the section on multicomponent fuels we shall further show that the existence of internal motion may qualitatively influence the combustion characteristics of multicomponent droplets.

## 6. Near- and super-critical combustion

Because of the enhanced combustion efficiency and intensity under high pressure, internal combustion engines operate under elevated pressures frequently in excess of the thermodynamic critical pressure of the liquid fuel. For example, while the critical pressures of diesel fuels are of the order of 20 atm, the pressure within diesel engines can range from 40 atm at the end of the compression stroke to twice that value at the peak combustion pressure. While these values seem to indicate that the droplet should undergo supercritical combustion early in its lifetime, considerations of the finite droplet heating rate and the dissolution of the permanent gases, which can raise the critical pressures of the fuel to the range of 40 to 60 atm, render it possible that the droplet actually attains criticality after it is mostly vaporized.



At elevated pressures various aspects of low-pressure droplet combustion need to be revised. The elevation of the liquid boiling point lengthens the droplet heating period and thereby its lifetime. The overall chemical reaction rate generally increases with pressure, hence making extinction more difficult but favoring the formation of such pollutants as  $\text{NO}_x$  and soot. As the critical state is approached, gas-phase compressibility becomes important, while the reduced surface tension enhances internal circulation and favors droplet deformation and breakup. The gas-phase quasi-steady assumption breaks down as the gas and liquid densities become comparable. Finally, at the critical state the distinction between gas and liquid vanishes and the phenomena of interest cease to belong to the area of droplet combustion.

## 7. Multicomponent droplet combustion

Much of the earlier studies on droplet combustion used pure fuels. However, recent developments in engine design and fuel formulation indicate that multicomponent effects will become progressively more important in the utilization of liquid fuels. Combustion processes within engines will be more tightly controlled to further improve efficiency and reduce emissions. The synthetic fuels derived from coal, tar sand, and oil shale will have more complex composition as well as higher and wider boiling point ranges. There also exists considerable interest in the utilization of such hybrid fuels as water/oil emulsions, alcohol/oil solutions and emulsions, and coal-oil mixtures. The widely different physical and chemical properties of the constituents of these hybrid fuels necessitates consideration of multicomponent effects in an essential way.

To understand heterogeneous multicomponent fuel combustion, either as a droplet or in some other forms (e.g. pool burning), the following three factors have to be considered.

- (i) The relative concentrations and volatilities of the liquid constituents, as would be expected.
- (ii) The miscibility of the liquid constituents. This controls the phase change characteristics. For example the partial vapor pressure of a miscible fuel blend can be greatly modified when it is emulsified with even a small quantity of water and changes into an immiscible mixture.
- (iii) The intensity of motion within the liquid. This influences the rate with which the liquid components can be brought to the surface at which gasification takes place.

The third point requires further amplification. First, it is obvious that no matter how volatile a liquid element is, it cannot gasify unless it is exposed at the droplet surface either through the passive mode of surface regression, or the active modes of diffusion and internal circulation. However, liquid-phase mass diffusion is an extremely slow process; its rate being one to two orders slower than that of surface regression. Therefore with it being the dominant active mode of transport, it is reasonable to expect that both the volatile and non-volatile liquid elements in the core of the droplet will be "trapped" during most of the droplet lifetime. Under this situation the relative volatilities of the individual components obviously cannot be the dominating factors in effecting gasification. On the other hand, in the presence of internal circulation, liquid-phase mass transport is facilitated such that the relative volatilities exert much stronger influence on the individual gasification rates.

Thus the combustion characteristics of a multicomponent droplet can be discussed in the two extreme rates of internal mixing, namely (a) a diffusion limit in which there is no motion within the droplet interior such that diffusion is the only active transport mode, and (b) a (somewhat artificial) distillation limit in which it is assumed that mixing occurs so fast that the states within the droplet interior are perpetually uniformized. Let us first discuss the combustion of miscible fuel blends in these two limits.

Because of diffusional resistance, it is reasonable to expect that the composition of the droplet inner core is practically not influenced by the surface gasification and therefore remains close to its initial value. However, since the volatile component has a relatively lower concentration at the surface, therefore there must exist a thin surface layer through which the composition rapidly changes<sup>12,13</sup>, as shown in Fig. 6. Furthermore, overall mass conservation requires that the fractional gasification rate of the  $i$ th species must be equal to its initial mass fraction. Therefore it is reasonable to expect that after the initial droplet heating period, a  $d^2$ -Law behavior should prevail for the droplet size history, as shown in Fig. 7.

The diffusional stratification of the concentration can lead to the occurrence of an interesting disruptive combustion phenomenon termed micro-explosion.<sup>13</sup> It is reasoned that since the droplet surface has a higher concentration of the non-volatile, high-boiling-point, component, and since the droplet temperature is controlled by its composition at the

surface, therefore the droplet can be heated to a high temperature. However, the droplet inner core is concentrated with the volatile, low-boiling-point, component. It is therefore possible that the inner core mixture can be heated to its limit of superheat and homogeneously nucleates. The subsequent internal pressure build-up is tremendous and causes the droplet to explode violently.

It has also been predicted that micro-explosion can occur only for an optimum range of mixture concentration; the non-volatile component is needed to drive up the droplet temperature while the volatile component is needed to facilitate homogeneous nucleation.<sup>14,15</sup> Furthermore, since the boiling point increases significantly with pressure while the homogeneous nucleation temperature is extremely insensitive to pressure variations, at least for pressures not close to critical, it is also suggested<sup>13</sup> that increasing pressure enhances the occurrence of micro-explosion. This is an attractive consideration for application in internal combustion engines.

The occurrence of micro-explosion and its compositional dependence have been experimentally verified<sup>16</sup>, although the pressure dependence has not been experimentally investigated.

The possible occurrence of micro-explosion offers interesting potential in the flexibility with fuel atomization. That is, fine atomization need not be the primary concern with designing the spraying process. In fact, it may be advantageous to have somewhat larger droplets which possess sufficient inertial for penetration into the combustor interior in order to achieve optimum charge distribution. Upon penetration, rapid gasification can then be effected through micro-explosion.

In the distillation limit<sup>17</sup> the perpetual uniformization of the droplet composition implies that the volatility-differentials should be the controlling factor. The gasification of the components should occur approximately sequentially according to their relative volatilities. Thus for components with sufficiently different volatilities a plot of  $d_s^2$  versus time should yield approximately linear segments of different slopes separated by sharp transition periods, during which the droplet temperature increases (Fig. 7). Such behavior has been experimentally verified. The droplet lifetime may or may not exceed that of the diffusion limit. It is also obvious that in the absence of diffusional stratification micro-explosion will not occur in this limit. Thus enhanced mixing, say in the form of internal circulation generated by external convection, tends to inhibit micro-explosion.

It may also be noted that the distillation limit is an artificial one. Recently more rigorous analyses<sup>18</sup> allowing for internal circulation show that the distillation limit can never be approached and that diffusional stratification prevails even under intense external convection. On the other hand experiments on droplet combustion subjected to either natural and/or forced convection do show distillation-like behavior even with mild convective intensity.<sup>3</sup> As of now no satisfactory explanation exists for this disagreement.

Next we discuss the combustion of water-in-oil (W/O) emulsions, which have been tested in a variety of combustors including the diesel engine, the gas turbine, and furnaces and boilers.<sup>19</sup> The results generally indicate a reduction in soot and  $\text{NO}_x$  emissions while those of CO and unburned hydrocarbons are somewhat increased. Change in the combustor efficiency on the basis of oil consumption is less clear; slight improvements and degradation have been reported depending on the state and type of the combustor, the testing procedure, and the properties of the emulsions used.

The main differences between an W/O emulsion and a miscible fuel blend is that the water micro-droplets do not diffuse and that the immiscibility property can significantly influence the phase equilibrium relation at the droplet surface. For example under equilibrium vaporization, which implicitly requires a distillation mode of internal transport, each immiscible component will vaporize independent of the presence and quantity of the other component. This implies that the boiling point of the emulsion is limited by the lower of the boiling points of these components. Thus the attainable temperature and the associated vapor pressure of a high-boiling-point oil can be greatly suppressed by adding only a small quantity of water. Micro-explosion obviously is not possible. On the other hand, in the absence of significant internal motion, it has been found<sup>20,21</sup> that micro-explosion again occurs and is actually more violent than that for a miscible fuel blend. This is reasonable because of the large amount of the superheated mass available within the water micro-droplets.

Finally we discuss the combustion of coal-oil-mixtures (COM), which offers a promising technology for coal utilization by mixing finely crushed coal in oil and then directly burn the coal-oil mixture in such stationary burners as furnaces and boilers. The concept is attractive in that it enables the direct substitution of oil by coal, that the crushing and mixing processes involved in its preparation are more economical than the energy-expensive coal-liquefaction and gasification processes, and that the mixture is still pumpable and

hence can be readily used in the conventional oil-fired combustors with minimum hardware modification.

The combustion characteristics of COM droplets again depend intimately on the extent of internal circulation. Internal bubbling and disruptive combustion should be facilitated because, with coal particles serving as potential heterogeneous nucleation sites, the droplet does not need to reach the high temperature required to initiate homogeneous nucleation. However, the intensity of explosion will be milder because of the reduced amount of superheat available.

Experimentally, sporadic, mild fragmentations have been observed for a suspended coal/diesel droplet burning in the quiescent, normal atmosphere.<sup>16</sup> The fragmentation becomes explosive with the addition of less than 5% water. However, these fragmentations can be completely suppressed<sup>22</sup> by increasing the extent of external convection produced either by upward blowing of hot gas or simply letting the COM droplet fall through a hot furnace. Therefore in the absence of fragmentation, all the coal particles originally present in the COM droplet are concentrated into a large coal particle agglomerate<sup>22</sup>, which requires a long burning time and is expected to be a serious problem with COM utilization in combustors with short residence times.

### 8. Droplet interaction

In the practical situation within a spray, any given droplet is surrounded by and therefore interacts with the rest of the droplet ensemble. Since the characteristic droplet separation distance can be of the same order as the flame size<sup>3</sup>, the intensity of interaction can be quite strong. In particular, for sufficiently short separation distances, the droplets will burn as a merged flame instead of individually.

To study interaction effects, it is necessary to solve Eqs. (3) and (10), together with the momentum conservation equation, for the three-dimensional flow configuration. If we make the thin-flame approximation and also assume weak convection, then the analysis simplifies to that of the Laplace Equation, of which many solution procedures exist. In the presence of convection, special solutions<sup>23-25</sup> have also been obtained.

Experimentally it has been demonstrated<sup>22</sup> that interaction reduces the droplet burning rate because of the competition for oxygen. d<sup>2</sup>-Law behavior obviously does not hold because of droplet regression and therefore the continuous variation of the droplet surface separation distance. The presence of buoyancy, however, can significantly increase the burning rate because of the synergistically-enhanced convective transport between droplets.<sup>26-28</sup>

The case of strongly convective situation is of special interest because of the influence of wake regions on neighboring droplets.<sup>29</sup> Another area of active research on droplet interaction is the Leidenfrost Phenomenon<sup>29</sup>, in which the droplet gasifies over a hot surface and exhibits a non-monotonic behavior in its lifetime with increasing surface temperature.

### 9. Concluding remarks

Presently the fundamental mechanism governing low-pressure, spherically-symmetric, single-component droplet combustion can be considered to be reasonably well understood. However, quantitative prediction of the burning characteristics is still inadequate, primarily as a result of transport property variations. This becomes serious during intense burning because the elevated flame temperature not only causes dissociation, but also introduces greater temperature and compositional variations in the transport properties. It would be of interest to conduct a numerical simulation of such a process, using realistic transport properties but simplified reaction schemes, and compare the predictions with the existing experimental data. Caution should be exercised in assessing the initial conditions which affect the droplet heating and fuel vapor accumulation processes.

The dynamics of a vaporizing droplet, with various intensities of interfacial mass flux, and the coupled problem of droplet vaporization under external convection, have not been adequately explored. Systematic studies assuming low, intermediate, and moderately high Reynolds number flows are all needed.

A detailed study of the droplet internal motion and transfer processes could also resolve the issue that while theoretical analysis on convective multicomponent droplet combustion shows non-uniform droplet concentration persists throughout the droplet lifetime, experimental results seem to indicate a batch distillation mode with the concentration perpetually uniformized.

The phenomenon of micro-explosion has potential to improve charge preparation and deserves further study. For miscible fuel blends the dependence of micro-explosion on the fuel composition and internal motion is sensitive and should be characterized. For W/O emulsions, emulsion stability, the optimum water droplet sizes, and the effect of pressure are the important problems.

High-pressure near-critical and super-critical combustion is a fertile area of research. The primary question here is whether the droplets can reach criticality before they have been substantially gasified. Many of the assumptions in modeling low-pressure droplet combustion break down near the critical state. The attainment of micro-explosion and coal-particle agglomeration also depends on whether criticality is reached before these events take place.

In view of the recent interest to conduct combustion experiments in the gravity-free Space-Lab environment, a candidate experiment is that of the combustion and micro-explosion of multicomponent droplets. This experiment cannot be easily and perfectly conducted on earth using conventional techniques. For example the suspension technique cannot be used because the suspension fibers can serve as heterogeneous nucleation sites to induce artificial micro-explosion. Freely-falling droplets experience forced convection and therefore internal circulation, whose intensity also continuously varies because of the changes in the droplet velocity and size. Finally, the presence of natural convection also induces internal motion. Thus only in a gravity-free environment can a stationary and convection-free experiment involving an unsuspended droplet be conducted.

Recent advances in computational techniques also allow the possibility of studying certain aspects of droplet combustion which are not easily amenable to analytical solutions. One example is the effects due to variable transport property values as just mentioned. The influence is especially strong in the liquid phase. For convective combustion numerical solution is also useful because of the lack of spherical symmetry, the presence of the complex flows, and the fact that relevant Reynolds numbers frequently are in the analytically difficult range of 1 to 100. During high pressure combustion much of the conventional assumptions describing droplet combustion break down (e.g. gas-phase quasi-steadiness and compressibility) such that numerical solutions again may be necessary. Finally, studies on droplet interaction may also find numerical approach useful because of the lack of symmetry in the problem.

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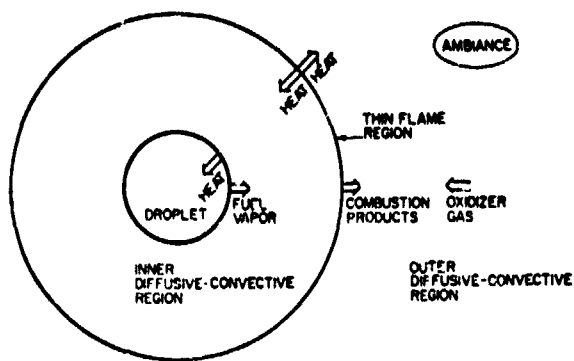


Figure 1a. Schematic showing spherically-symmetric droplet combustion.

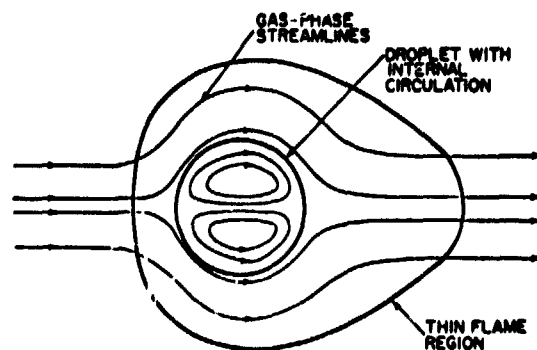


Figure 1b. Schematic showing convective droplet combustion without flow separation.

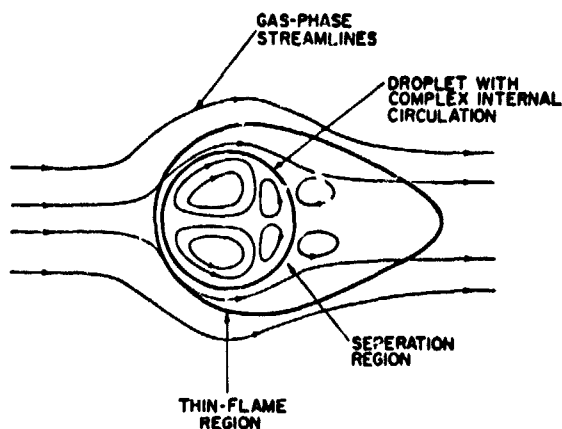


Figure 1c. Schematic showing convective droplet combustion with flow separation.

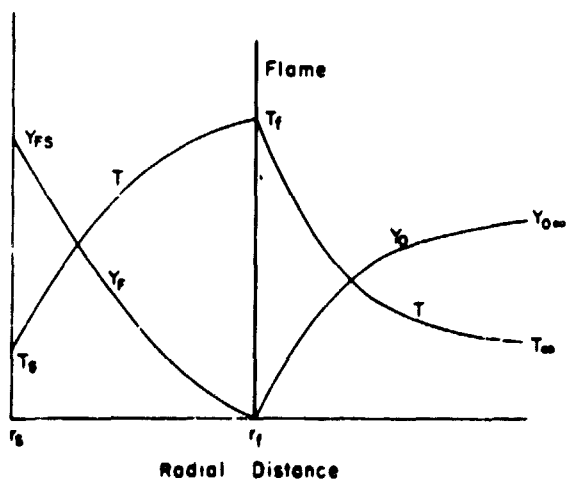


Figure 2a. Temperature and concentration profiles during droplet combustion in the flame-sheet limit.

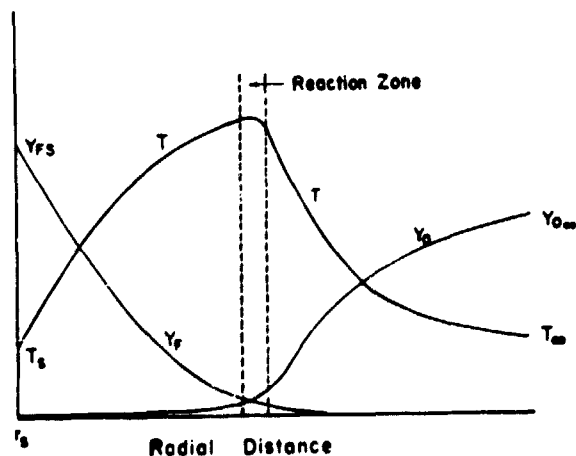


Figure 2b. Temperature and concentration profiles during droplet combustion with finite rate kinetics.

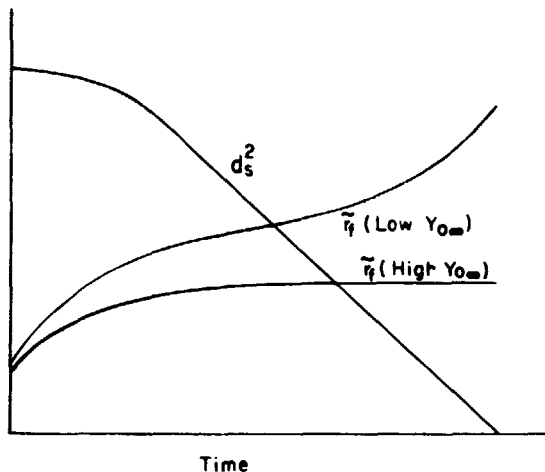


Figure 3. Experimental results on the temporal variations of diameter-squared,  $d_s^2$ , and flame-front stand-off ratio,  $\tilde{r}_f = r_f/r_s$ , during spherically-symmetric combustion.

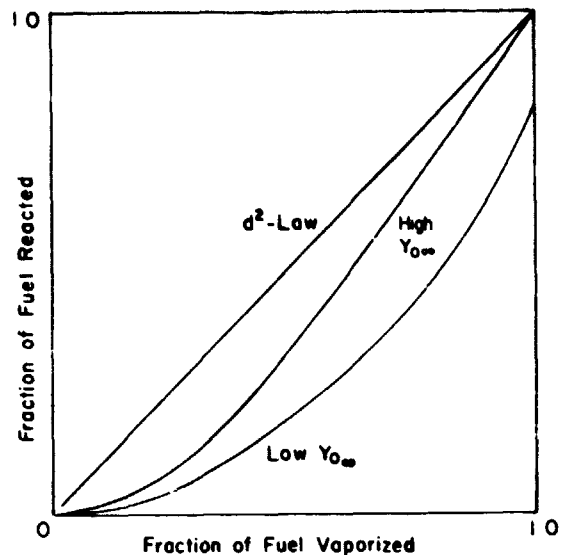


Figure 4. Fractional amount of fuel reacted as function of fractional amount vaporized, illustrating the importance of fuel vapor accumulation.

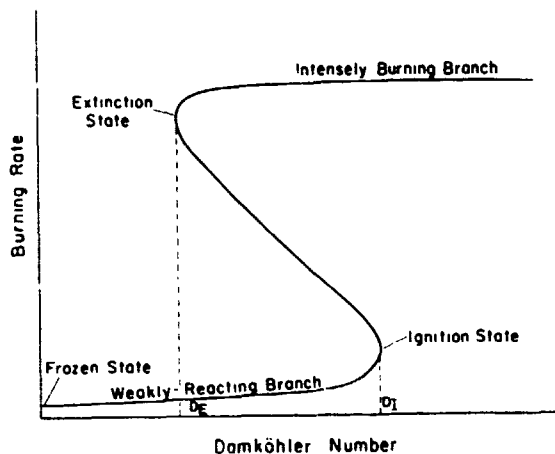


Figure 5. S-shaped response curve representing all possible solutions of quasi-steady droplet burning with finite reaction rate.

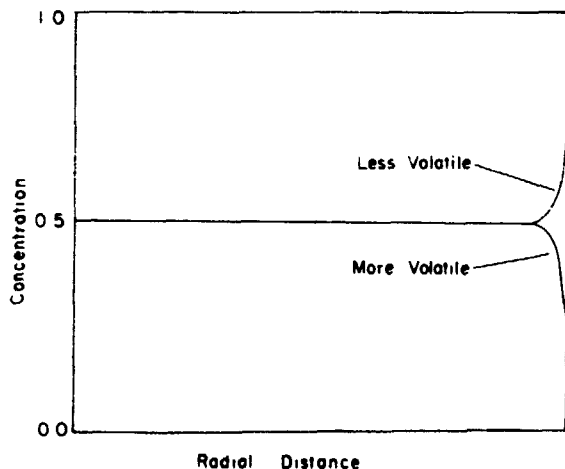


Figure 6. Droplet concentration profile for a bi-component droplet with initially equal concentrations.

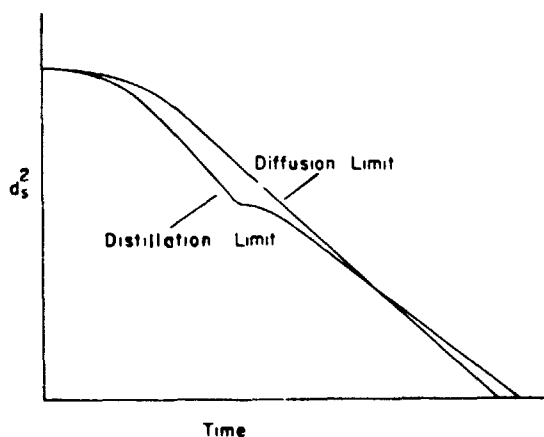


Figure 7. Temporal variation of the droplet surface area in the two limits of internal mass transport.